Thermal Outgassing of DC 93-500, a TWT Encapsulant

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This technical report has been reviewed and is approved for publication.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Approved

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The silicone traveling wave tube (TWT) encapsulant DC 93-500 has been subjected to thermal/vacuum analyses to verify its thermal stability and determine the extent of outgassing at the most severe expected operating conditions. Some limited comparisons have been made with a potential substitute encapsulant, Sylgard-184.

The thermal stability of 93-500 is entirely satisfactory under the conditions studied (120°C, vacuum, long term).

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

Significant outgassing was detected. Sufficient characterization was carried out to identify the mechanism of outgassing as being due to hydrolysis of silane by residual water in 93-500 base resin. The reaction produces volatile mono-vinyl silanol with appreciable quantities of hydrogen as a byproduct.

The possible influence of the outgassing on the ultimate mechanical properties is discussed, as well as the potential for contamination of adjacent optical surfaces, and the possibility of the reaction as a source of hydrogen within the tubes. Firm answers to the additional questions raised by this study are not presently available.

CONTENTS

FIGURES

FIGURES (Continued)

I. INTRODUCTION

Polymeric encapsulants for electrical and electronic components can be useful and effective in providing electrical and thermal insulation only insofar as: (1) the encapsulant retains its chemical and mechanical integrity, and (2) it maintains a strong adhesive bond to its substrate. These characteristics of a polymer depend, in part, on its stability in the particular environment with respect to chemical change and evolution of gases or volatiles.

Specifically, for traveling-wave tubes (TWTs) in the region of the collector, a possible failure mode involving corona discharge has been identified as being due to gas evolution. Evolution of gas may be due to thermal degradation or to simple outgassing. In either case, gas evolution may: (1) provide a medium for corona discharge, (2) be a source of the hydrogen which has occasionally been detected within TWTs, or (3) adversely influence the mechanical properties of the encapsulant.

This report primarily addresses the thermal outgassing behavior of DC 93-500, the chief candidate encapsulant in the Watkins-Johnson (W-J) TWT design. It includes some comparative data with Sylgard-184, a silicone analog which W-J is using, in part, as a substitute for qualifying the initial production tubes. An earlier candidate, a polyurethane resin, Solithane 113, is discussed in a separate report.[1]

Although it cannot be stated with certainty that 93-500 and Sylgard-184 are equivalent materials, some justification can be made for the direct substitution of these two materials in the qualification program. Factors to consider are: the high cost (~$550/lb) of 93-500, the long leadtime for its procurement, and its limited shelf life. These factors complicate the logistics of operating with 93-500. In favor of using Sylgard-184, there is: (1) the

[1] C. A. Gaulin, et al., Long-Term Thermal Stability of Solithane, a Candidate TWT Encapsulant, TR-0079(4402)-1, The Aerospace Corp., El Segundo, Calif. (February 1979).

vendor's (Dow Corning Corp., Midland, Mich.) assurance that the two materials are manufactured from the identical base resin, (2) a near equivalence of chemical and physical properties, cured and uncured, and (3) relative ease of procurement. The vendor further states that 93-500 is Sylgard-184 processed to reduce the quantity of volatiles. Both materials use the identical curing agent.

In the present work, thermogravimetric analysis (TGA), both programmed and isothermal, has been used to arrive at quantitative estimates of the outgassing rates of 93-500 and Sylgard-184. Also, 93-500 has been exposed to the maximum expected operating temperature in the collector region (120°C) over a long period of time (to 440 hr), and a quadrupole mass analyzer was used to identify the product gases and volatiles. These experiments permit a description of the mechanism of volatiles production in 93-500 which may also be applicable (though quantitatively different) to Sylgard-184.

II. EXPERIMENT DESCRIPTION

The TGA experiments were carried out in an apparatus equipped with a Cahn Microbalance. The apparatus is capable of operation in vacuum (to 10^{-6} torr) or in static or flowing gas. These experiments included dynamic (programmed temperature to 200°C) weight loss measurements in vacuum and in static air. They also included isothermal measurements at 120°C to 100 hr in vacuum and in static air.

Thermal aging was carried out in a chamber built for this purpose (Fig. 1), attached to the source inlet of an Ultek Model 150 quadrupole mass analyzer. Additional details are given in Ref. 1. The aging chamber was initially evacuated to $\sim 10^{-7}$ torr, and the cured 93-500 samples, bonded to Al_2O_3, were maintained at 120°C. The evolved gases and volatiles were sampled through a Granville-Phillips leak valve to a source pressure of $5\text{-}7 \times 10^{-7}$ torr. Samples were taken and analyzed at 48, 144, and 240 hr. The evolved gases were pumped away following each analysis.

III. EXPERIMENTAL RESULTS

The TGA of Sylgard-184, programmed in air, is reproduced in Fig. 2. A comparable TGA in vacuum is shown in Fig. 3. It is evident that outgassing is a significant factor in this material. The onset of outgassing at $<50^{\circ}C$ in vacuum is indicative of some extremely volatile residual components. The volatiles account for nearly 1.7 wt% up to 200°C. Under isothermal conditions at 120°C, similar but greatly enhanced outgassing was recorded. The TGA in Fig. 4 shows outgassing in air atmosphere at a constant 120°C over a 100-hr period. The comparable result for the experiment in vacuum is shown in Fig. 5. In both instances, outgassing begins immediately and apparently reaches a constant rate at 100 hr, but is not ended. The maximum weight loss observed occurred in vacuum and amounted to 2.7 wt%. In contrast to the preceding, the TGAs for the formula 93-500 show appreciably reduced weight loss. In a programmed experiment in vacuum at 4°C/min (Fig. 6), ultimate weight loss to 200°C amounted to 0.2 wt%. The isothermal experiment at 120°C in vacuum (Fig. 7) shows that a constant rate of outgassing is attained at about 10 hr, and the 100-hr weight loss is reduced by a factor of five, relative to Sylgard, to about 0.45 wt%.

The mass spectrum of the outgassing products from the aging experiments, sampled at 48 hr, is shown in Figs. 8 and 9. The principal masses recorded occurred at m/e = 2, 15, 16, 28, 59, and 73. Figures 10 and 11 are the comparable spectra of the same sample at 144 hr, and Fig. 12 at 240 hr. The same masses were recorded in about the same proportions except that, in the latter, the ratio of m/e 59 to 73 is inverted. The pressure of the gases admitted to the spectrometer was held close to constant. The spectrum suggests that the composition of the gases did not change greatly with time. Quantitatively, also, the intensities of the peaks are in reasonable agreement with the TGA isothermal curve (Fig. 7) where the latter appears to indicate a constant outgassing rate. At each instance when the gas was

sampled, a broader mass range was also scanned, but no appreciable quantities of higher mass peaks were recorded. These spectra are exemplified by Figs. 9 and 11.

Initially, a tentative interpretation of these spectra was suggested which attributed the observed m/e 59 and 73 peaks to evolution of aliphatic ester from incompletely dried primer (DC Q3-6060).[2] This interpretation was based solely on inspection of atlases of mass spectral data that indicated one might expect peaks for

$$CH_3\,\overset{\overset{O}{\|}}{C}\,-\,O\,- \qquad 59$$

and

$$CH_3\,-\,\overset{\overset{O}{\|}}{C}\,-\,O\,-\,CH_2 \text{ or } C_4H_9\,-\,O\,- \qquad 73$$

characteristic of esters in conventional magnetic sector mass spectrometers. Furthermore, testing the odor of the primer clearly indicated the presence of esters, probably a mixture of ethyl and amyl acetates. Subsequent calibration of the quadrupole and additional experiments show that the above preliminary interpretation was premature and clearly was incorrect.

More recently, the spectra in the quadrupole of ethyl acetate, butyl acetate, and pentyl (amyl) acetate were examined. These are reproduced in Figs. 13, 14, and 15, respectively. In no instance were either m/e 59 or 73 detected. Comparing the spectrum of DC Q3-6060 primer, Figs. 16 and 17, there is a fair degree of correspondence, confirming the original qualitative identification of esters carried out by sniffology only. However, it is clear that aliphatic esters from the primer have no role in the outgassing of 93-500.

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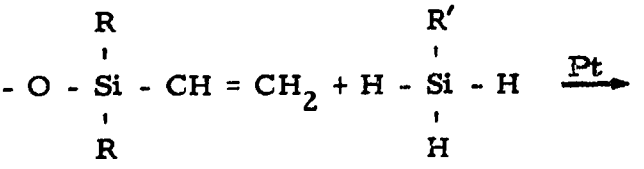
[2] F. M. Wachi, et al., Investigation of TWT Technology Problems: II: Watkins-Johnson TWTs, The Aerospace Corp., El Segundo, Calif. (Report in preparation).

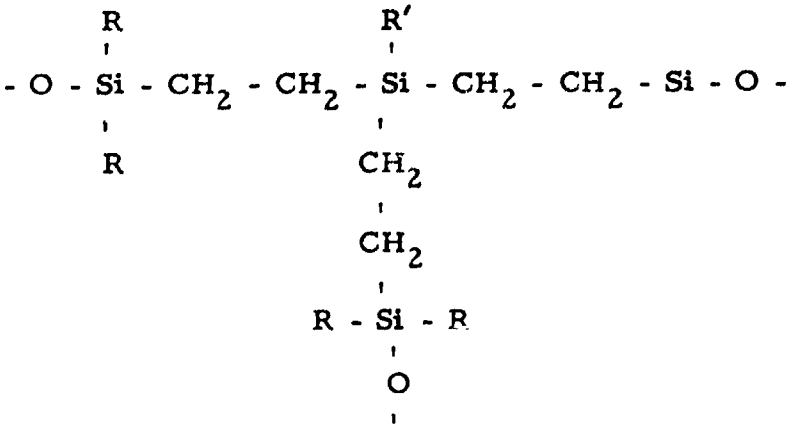
The raw ingredients of the cured polymer, namely 93-500 base resin and 93-500 curing agent, were also examined in the quadrupole. Figures 18, 19, and 20 show no large masses at 59 or 73. The curing agent contains a trace of 59, but principal masses at 43 and 45. The most significant peaks in the encapsulant base resin are m/e 17 and 18, attributed to residual H_2O. Based on these findings and armed with the knowledge that (1) curing agents for silicone addition polymers contain one or more silanes, and (2) that silanes are hydrolytically unstable, a quasi-model reaction between 93-500 curing agent and a stoichiometric quantity of water was carried out. After heating the mixture for about an hour at the boiling point of water (100°C), a sample of the product vapors was admitted to the quadrupole. The resultant spectrum, Fig. 21, clearly shows the 59 and 73 peaks characteristic of the cured resin. The implication of these results is that these species when seen in thermally aged DC-93-500 are the reaction product of residual water in the base encapsulant with a silane in the curing agent.

IV. DISCUSSION

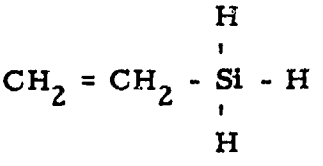
The polymerization (cure) reaction of DC 93-500 proceeds by an addition reaction that can be viewed generally as follows:

Silicone Addition Reaction





The observed results in the analyses are best interpreted on the basis that DC 93-500 curing agent consists primarily of vinyl silane:



M. W. 59

In the quadrupole mass spectrum it is seen predominantly as fragments (fragmentation ≈ $\int$):

$$CH_2 \not\!\!\int CH_2 - \overset{H}{\underset{H}{Si}} - H \qquad \text{m/e 45}$$

and

$$CH_2 \not\!\!\int CH_2 - \overset{H}{\underset{H}{Si}} \int H \qquad \text{m/e 43}$$

Due to its high intrinsic reactivity with water (hydrolytic instability), a hydrogen atom is readily replaced by -OH, resulting in the production of a silanol:

$$CH_2 = CH_2 - \overset{H}{\underset{H}{Si}} - OH \qquad \text{M.W. 74}$$

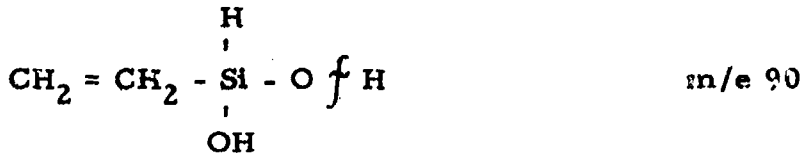
observed fragments,

$$CH \not\!\!\int CH_2 - \overset{H}{\underset{H}{Si}} - O \int H \qquad \text{m/e 59}$$

and

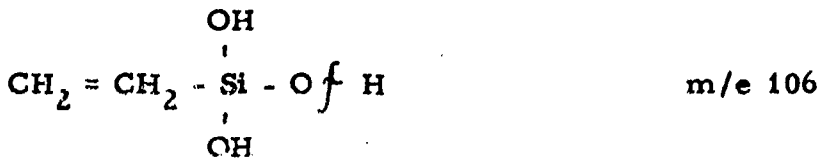
$$CH_2 = CH_2 - \overset{H}{\underset{H}{Si}} - O \int H \qquad \text{m/e 73}$$

The fact that neither m/e 90 or 106 was observed, corresponding to



m/e 90

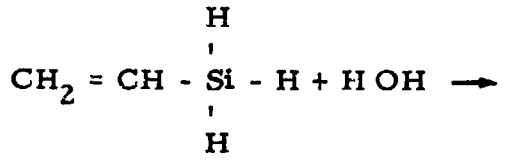
or

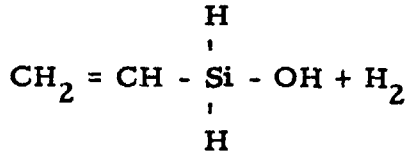


m/e 106

indicates that the primary hydrogen site is readily hydrolyzed, but the second and third hydrogen sites would hydrolyze only with much greater difficulty.

Considering the hydrolysis reaction:





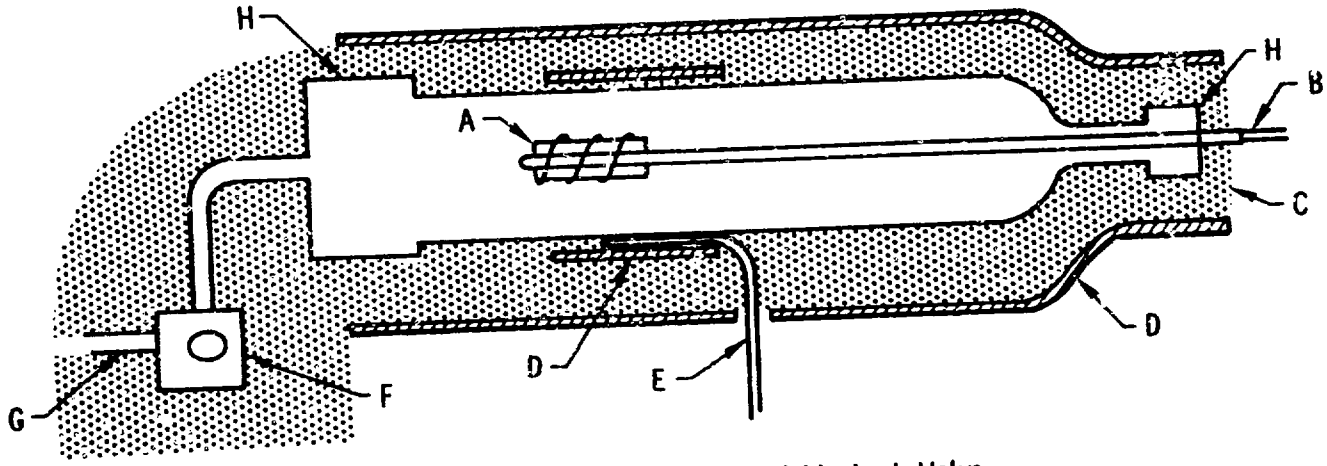
several consequences are evident.

a. Hydrolysis of silane by residual H_2O in the base encapsulant partially deactivates the curing agent. This suggests that an excess of silane would be needed to fully develop the properties (due to crosslinking) in the final cured product. However, excess silane is undesirable due to its own inherent volatility. The extent to which the final properties are affected by this hydrolysis are not understood. They might be determined by a parametric study in which the water and silane content were carefully and systematically varied.

b. The hydrolysis reaction generates volatile condensable silanol which, within the time limit studied (240 hr) continuously outgases at a nearly constant rate. The silanol might initially act as a plasticizer in the encapsulant, but its eventual removal could influence the ultimate properties of the material. Also, it is not known whether the presence of this volatile compound might degrade the performance of nearby optical components.

c. The byproduct of the hydrolysis reaction is hydrogen. Hydrogen has been found within certain TWTs in appreciable quantities. Some other mechanisms of hydrogen introduction into the tubes have been proposed and are being studied, but, at present, a mechanism based on evolution from the curing agent/H_2O reaction, and subsequent diffusion through Kovar parts, cannot be entirely ruled out.

Although this study has raised several questions regarding the consequences of outgassing of DC 93-500, nothing in the study would suggest thermal instability in the system. Under the conditions used in the experiments, elevated temperature stability of 93-500 is quite satisfactory.



A Sample
B Thermocouple to Recorder
C Heater Tape
D Pyrex Tape
E Thermocouple to Controller
F Variable Leak Valve
G Sampling Line to Quadrupole Mass Spectrometer and Ion Gauge
H Vacuum Fittings

not to scale

Figure 1. Schematic of Experimental Apparatus for Polymer Thermal Stability Study

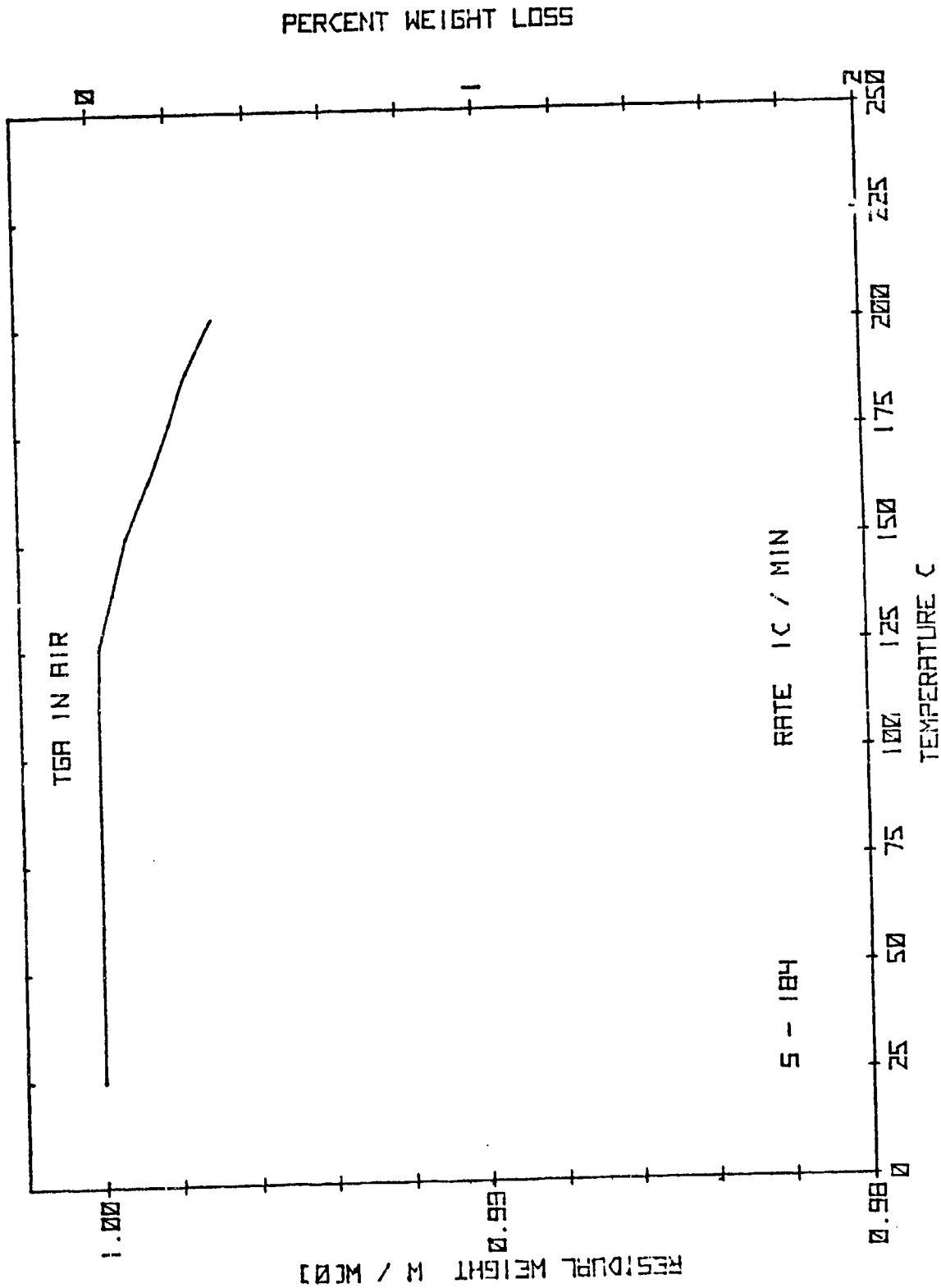


Figure 2. Dynamic Thermogravimetry of Sylgard-184 in Air

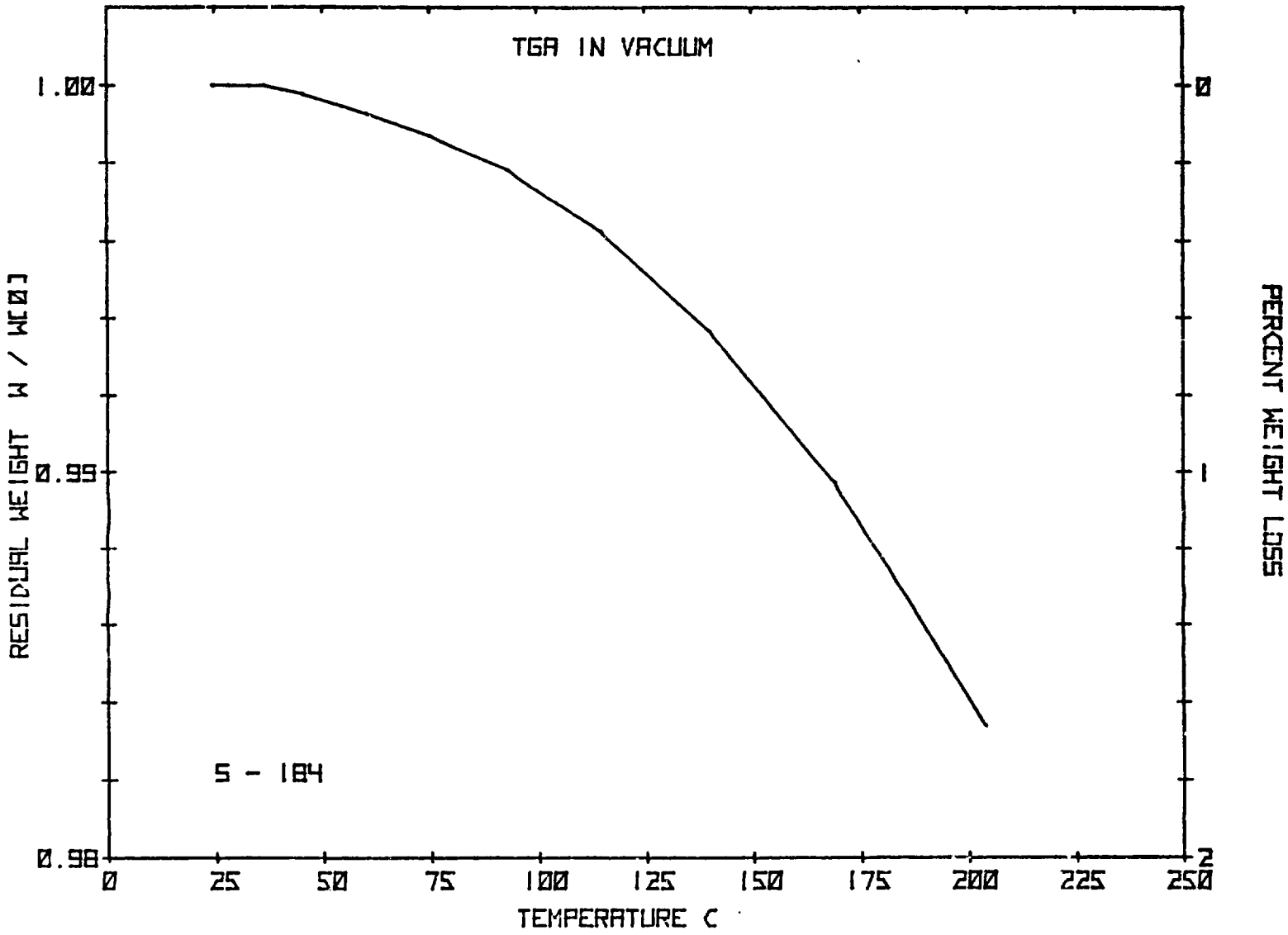


Figure 3. Dynamic Thermogravimetry of Sylgard-184 in Vacuum

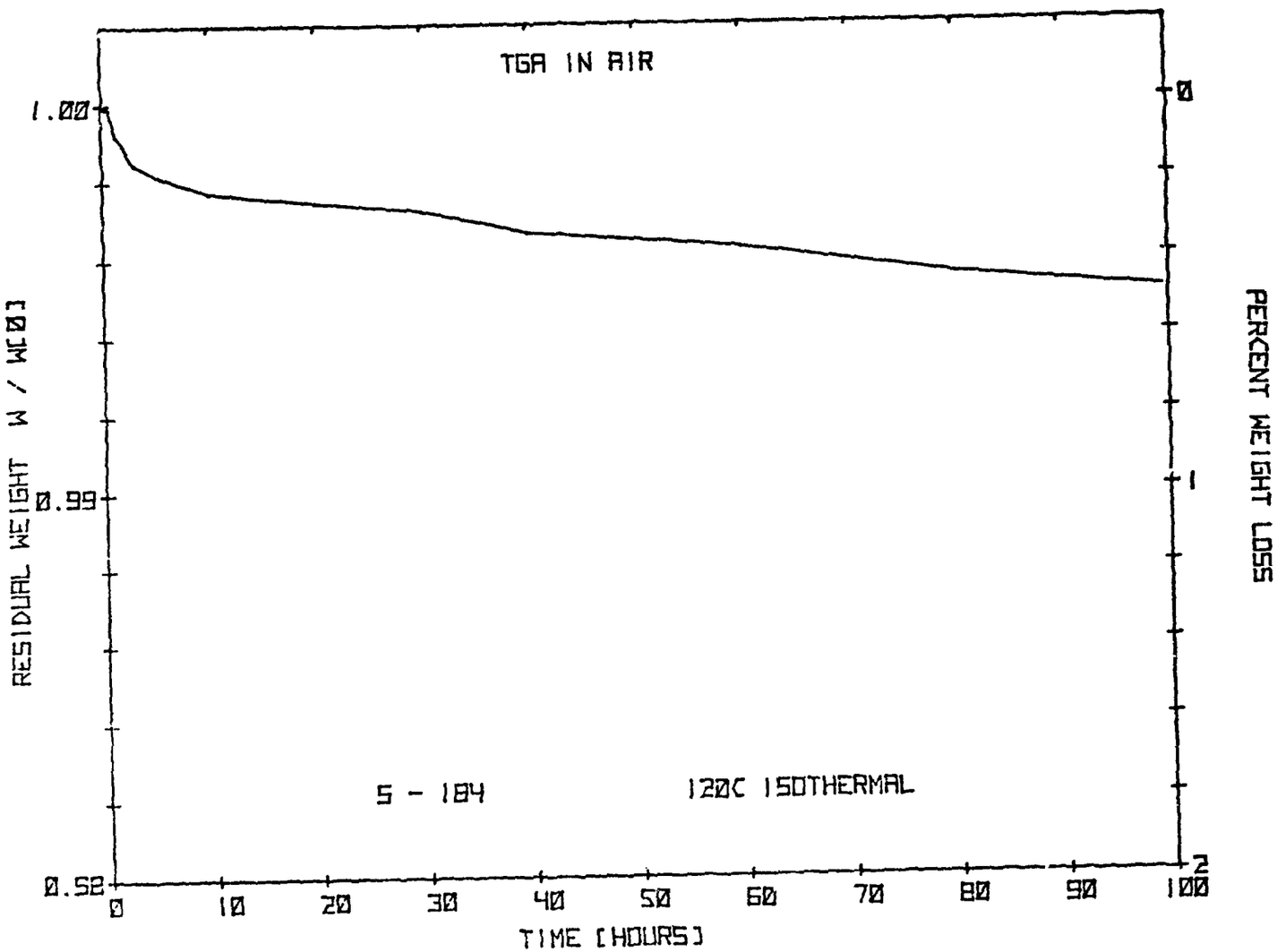


Figure 4. Isothermal Thermogravimetry of Sylgard-184 in Air at 120°C

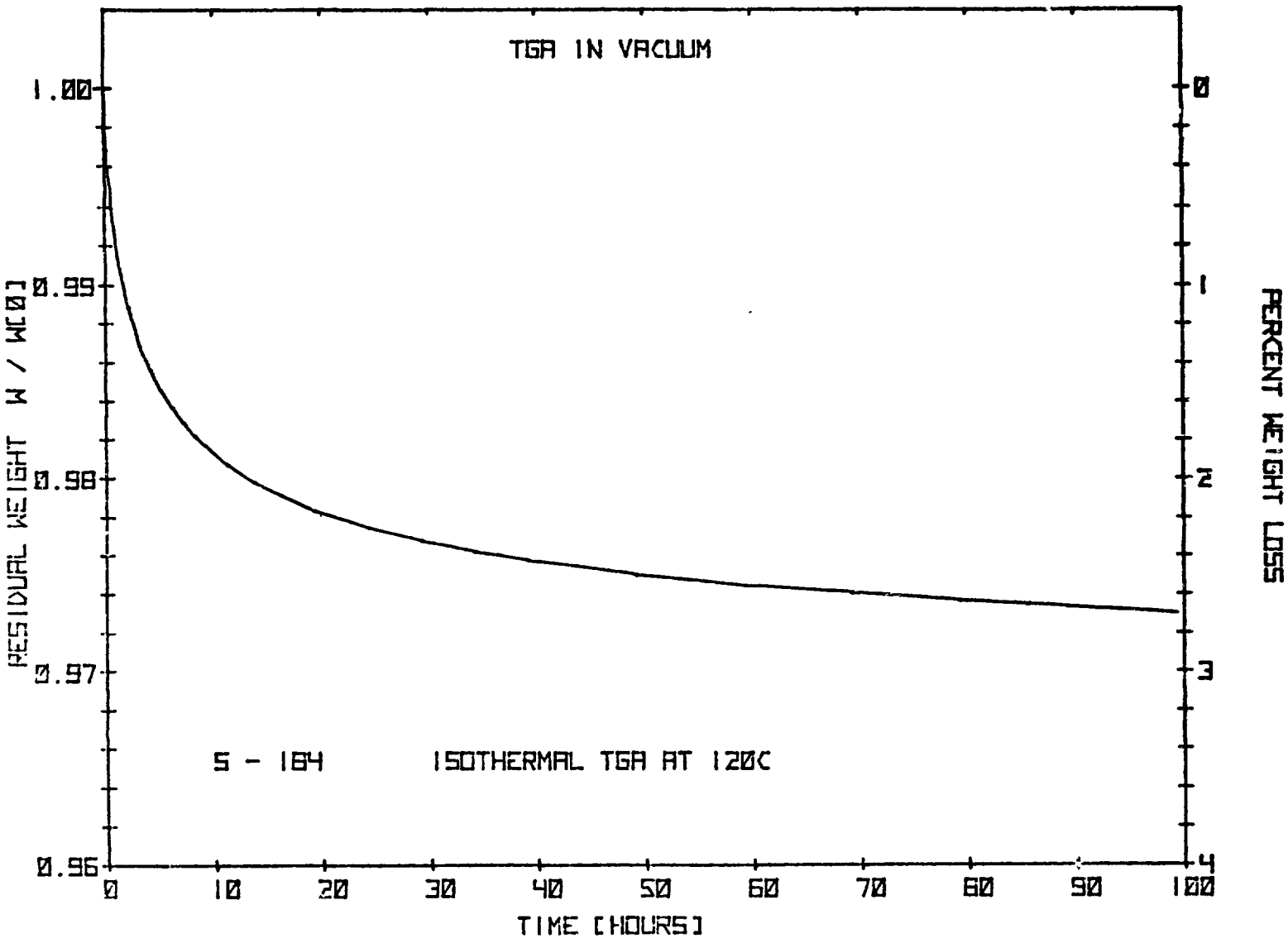


Figure 5. Isothermal Thermogravimetry of Sylgard-184 in Vacuum at 120°C

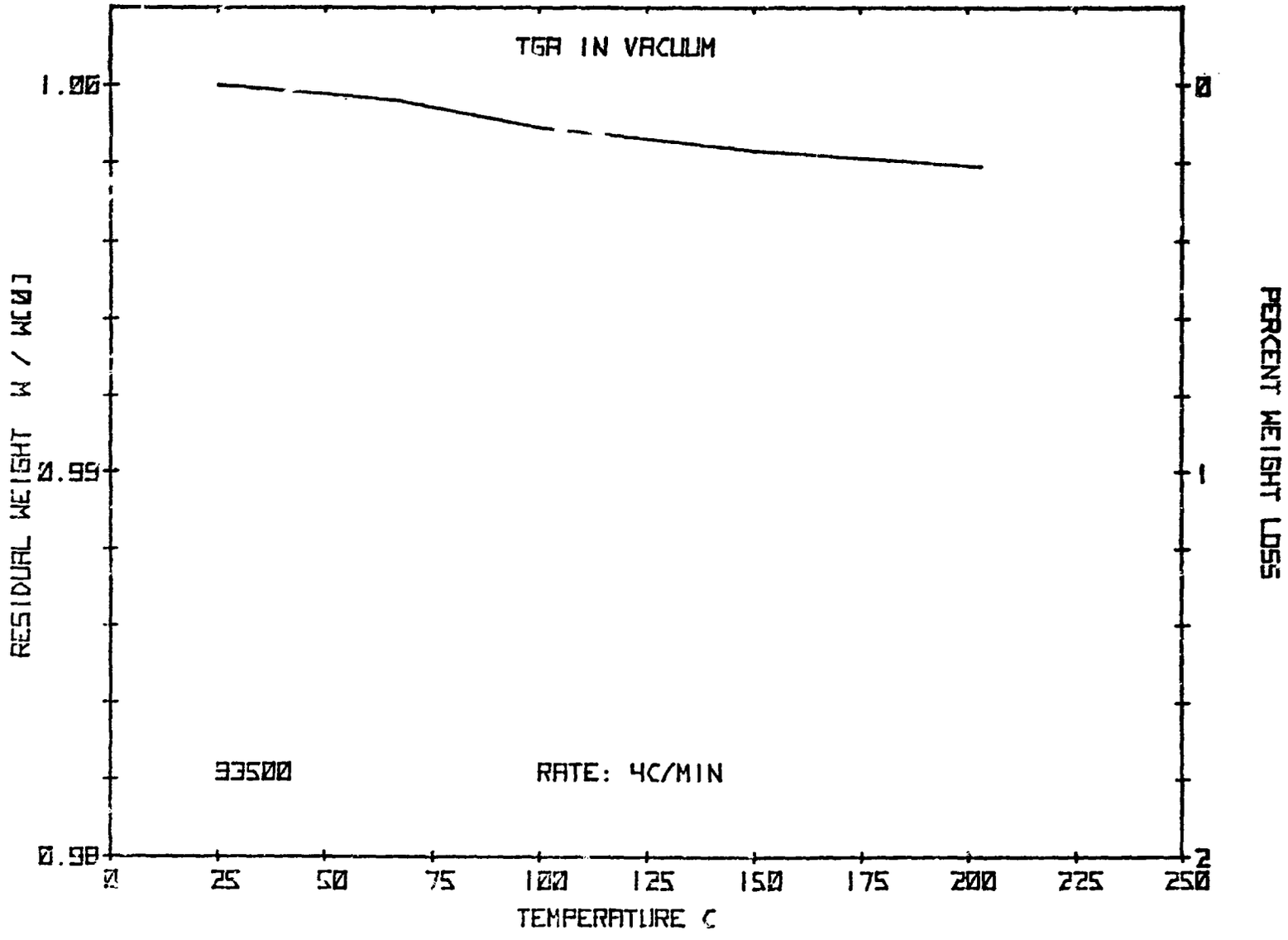


Figure 6. Dynamic Thermogravimetry of DC 93-500 in Vacuum

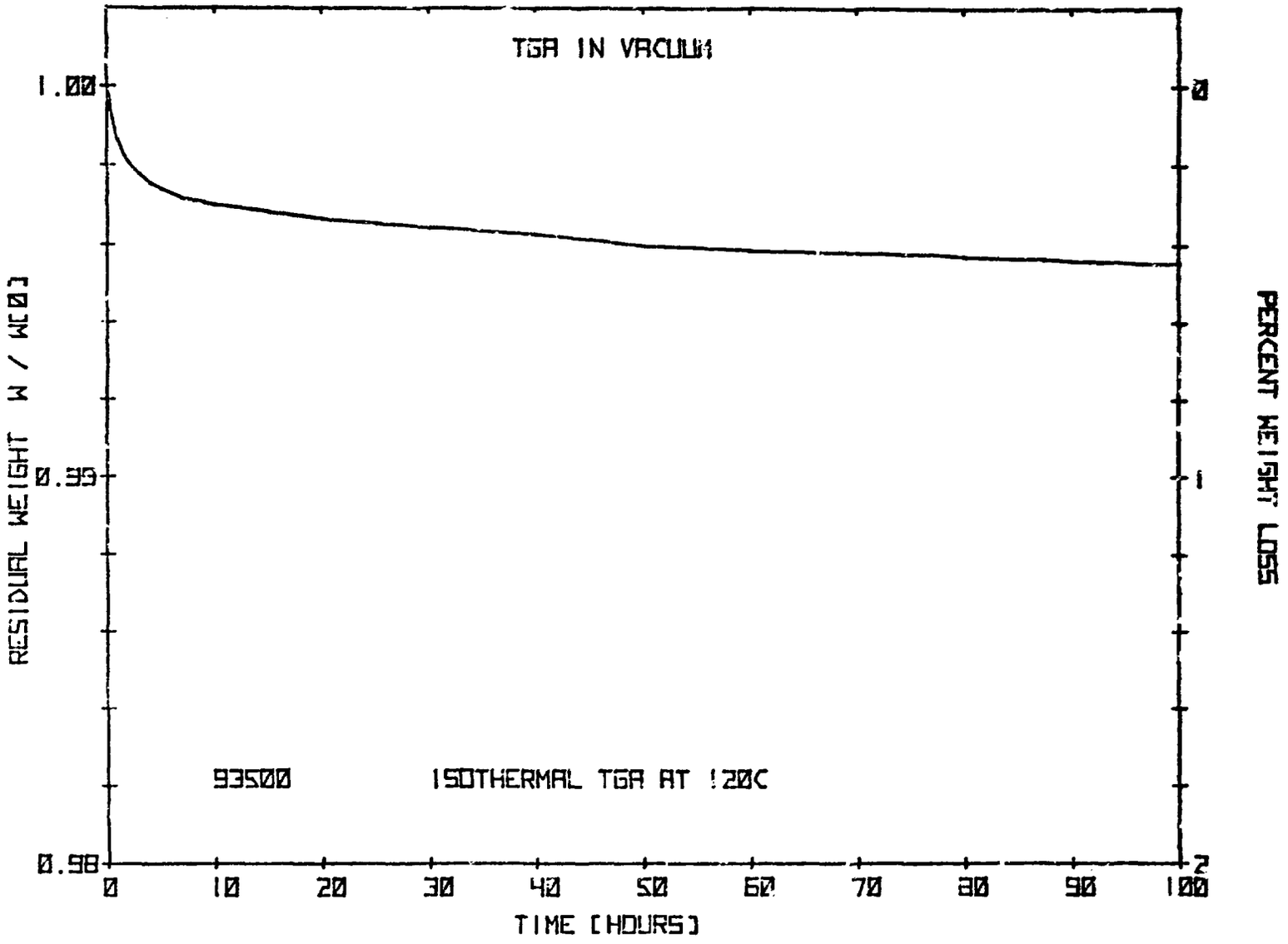


Figure 7. Isothermal Thermogravimetry of DC 93-500 in Vacuum at 120°C

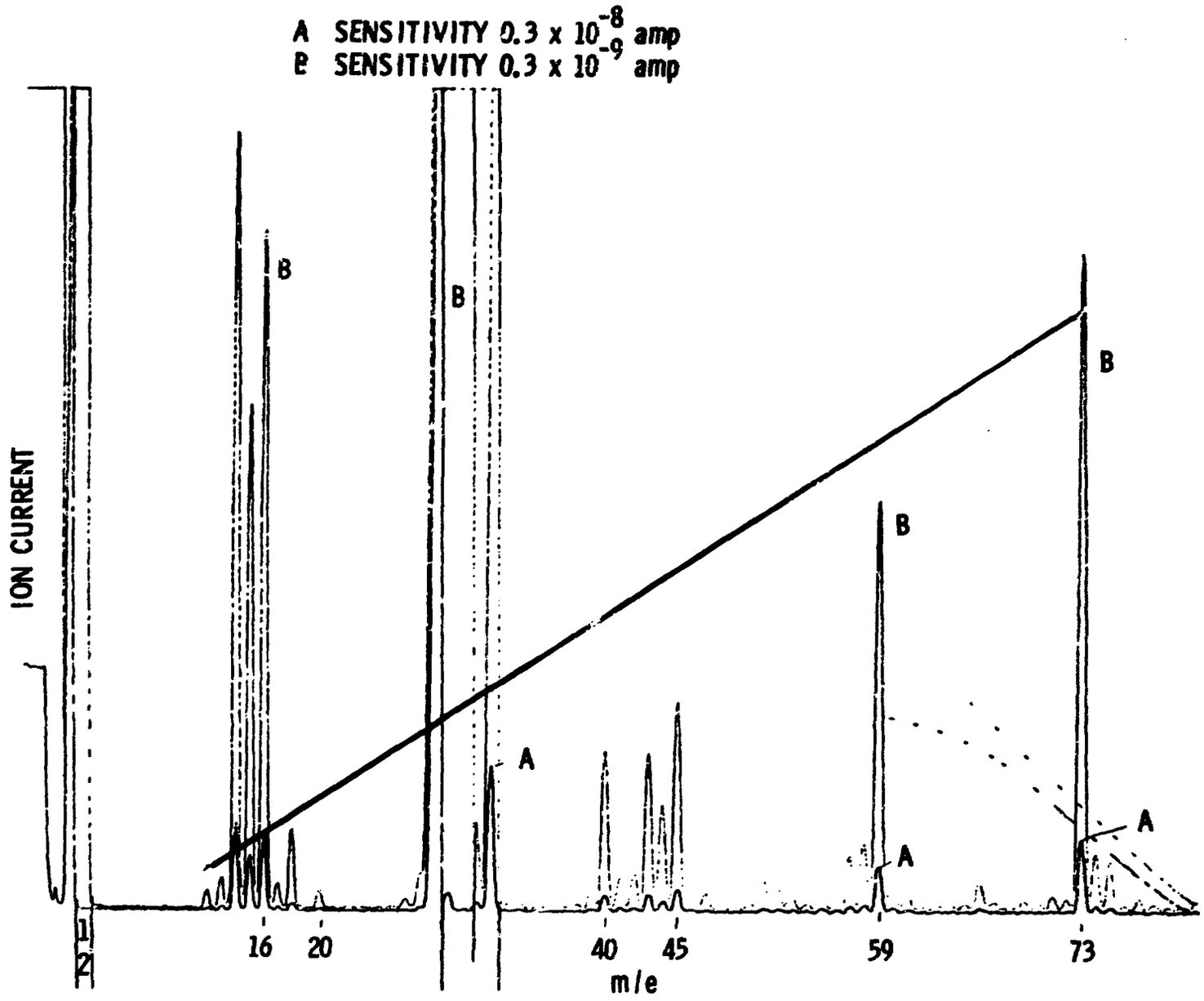


Figure 8. Quadrupole Mass Spectrum of Volatiles from Thermally Aged DC 93-500 at 4[illegible] hr

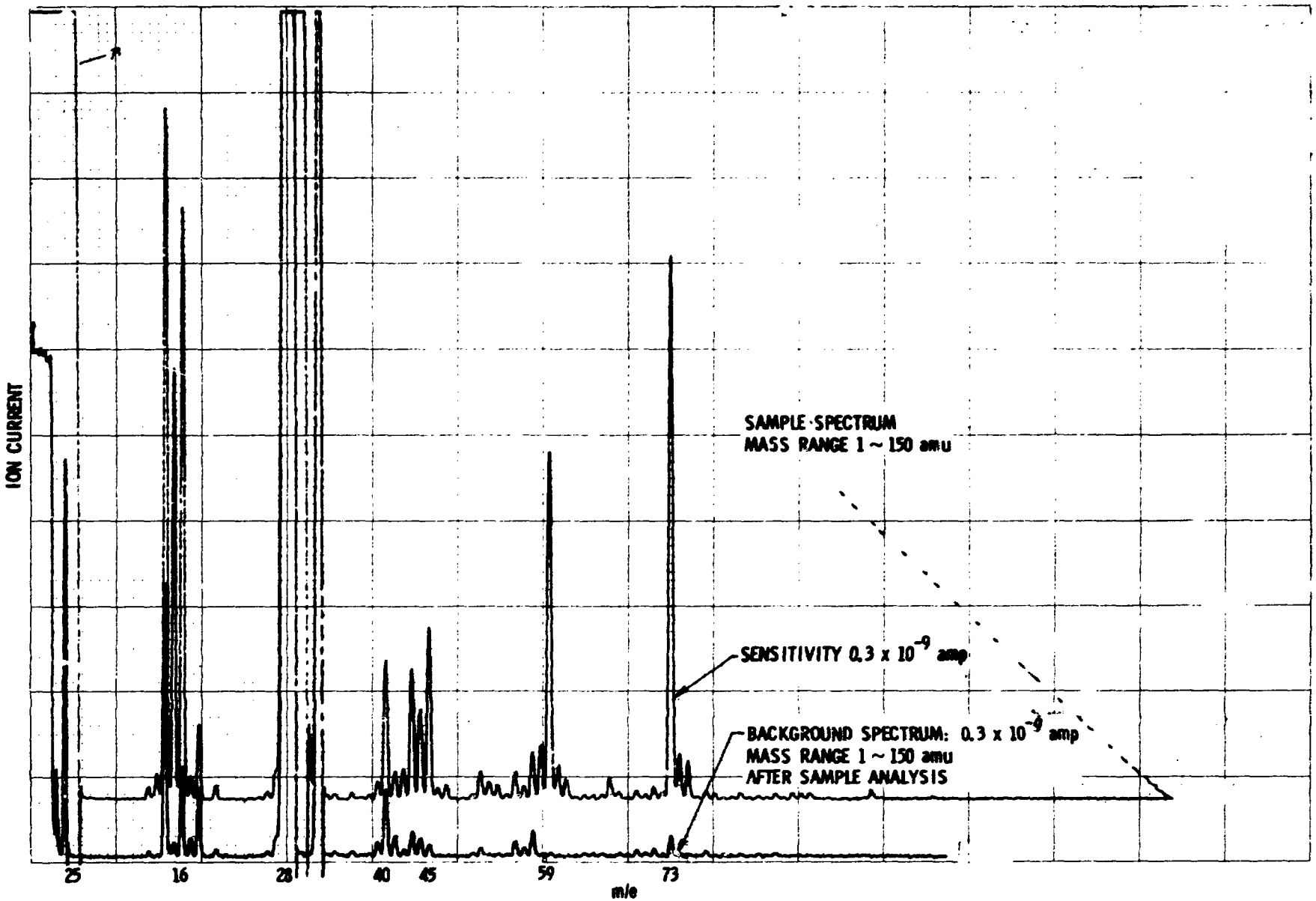


Figure 9. Quadrupole Mass Spectrum of Volatiles from Thermally Aged DC 93-500 at 48 hr

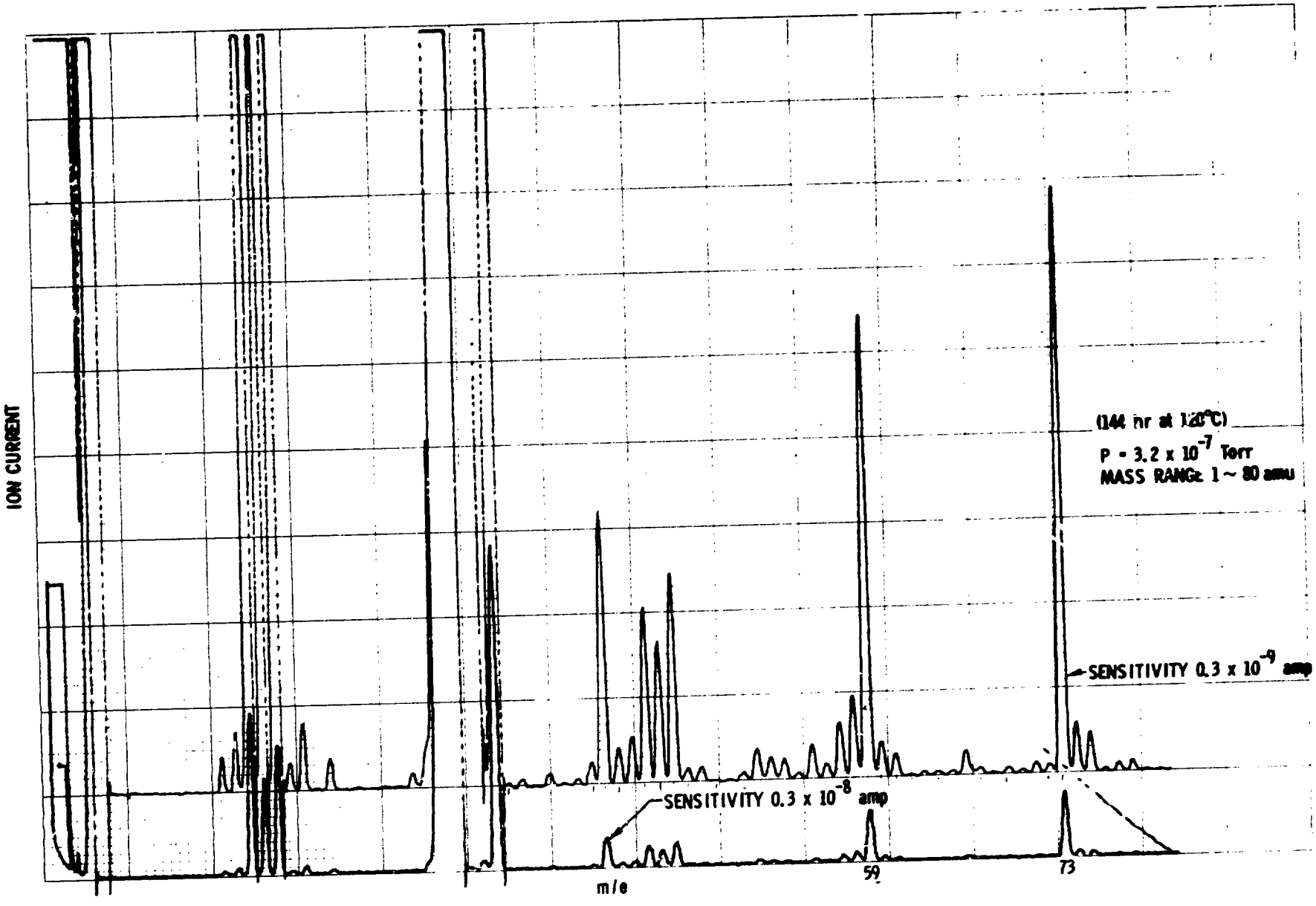


Figure 10. Quadrupole Mass Spectrum of Volatiles from Thermally Aged DC 93-500 at 144 hr

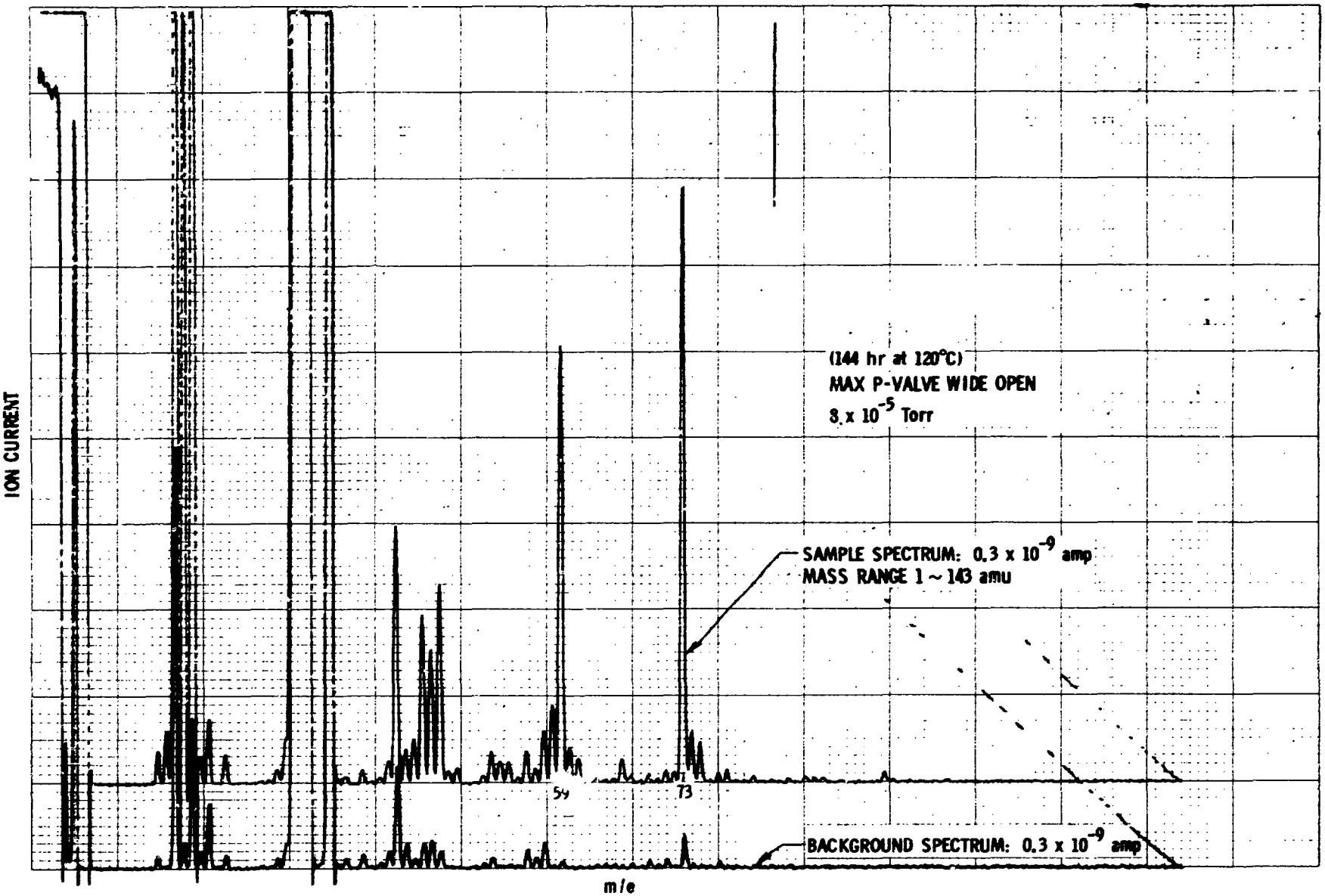


Figure 11. Quadrupole Mass Spectrum of Volatiles from Thermally Aged DC 93-500 at 144 hr

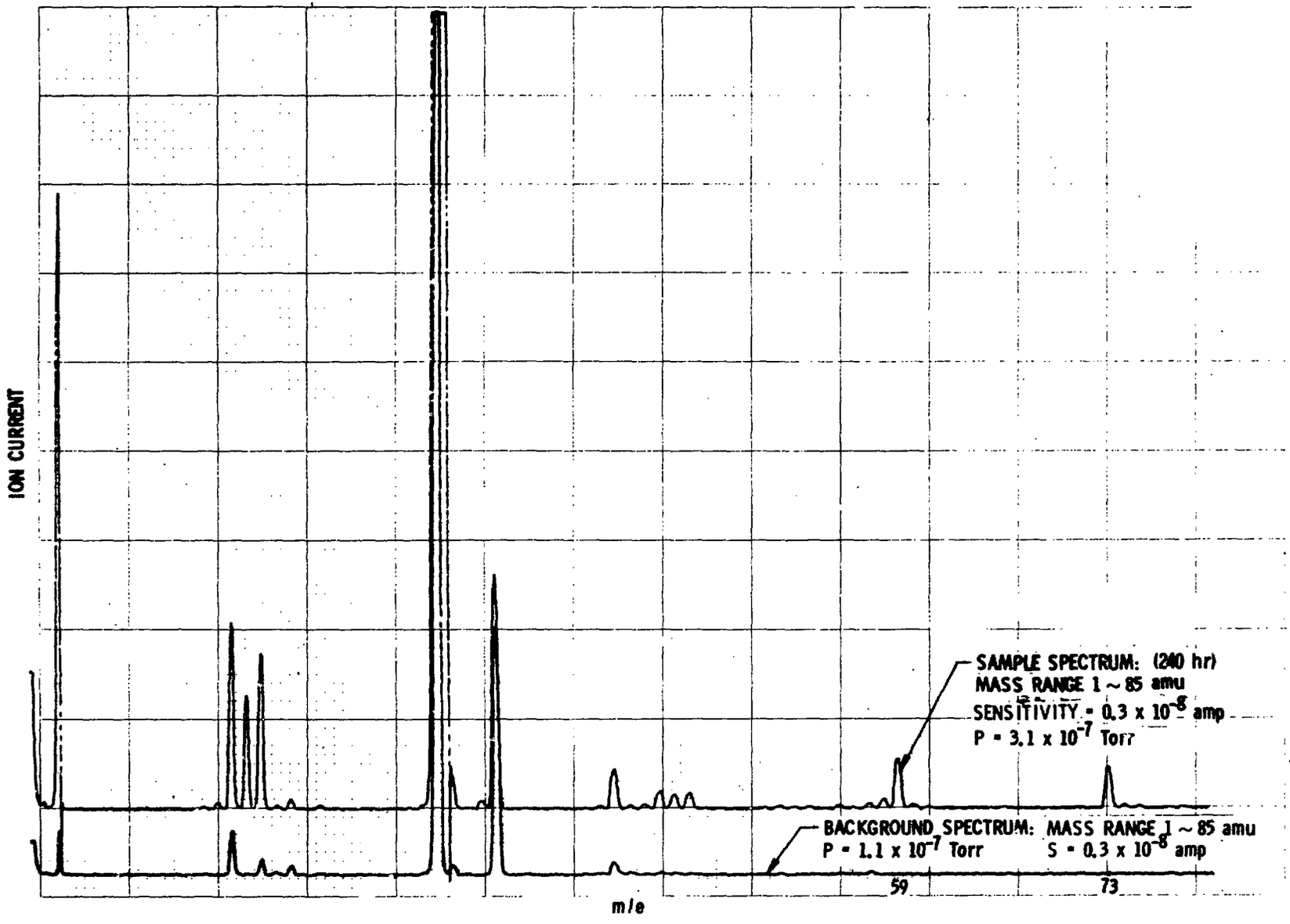


Figure 12. Quadrupole Mass Spectrum of Volatiles from Thermally Aged DC 93-500 at 240 hr

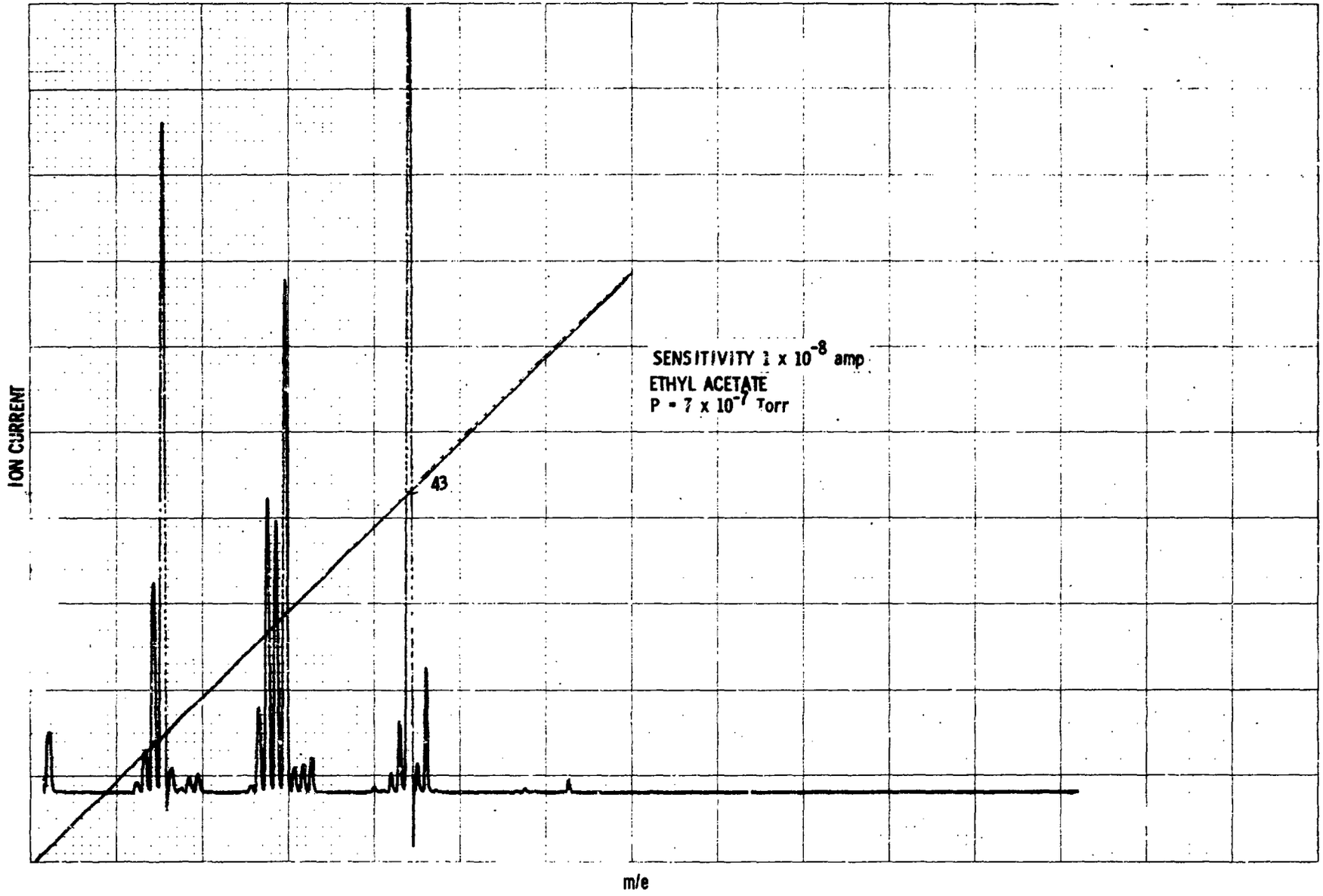


Figure 13. Quadrupole Mass Spectrum of Ethyl Acetate

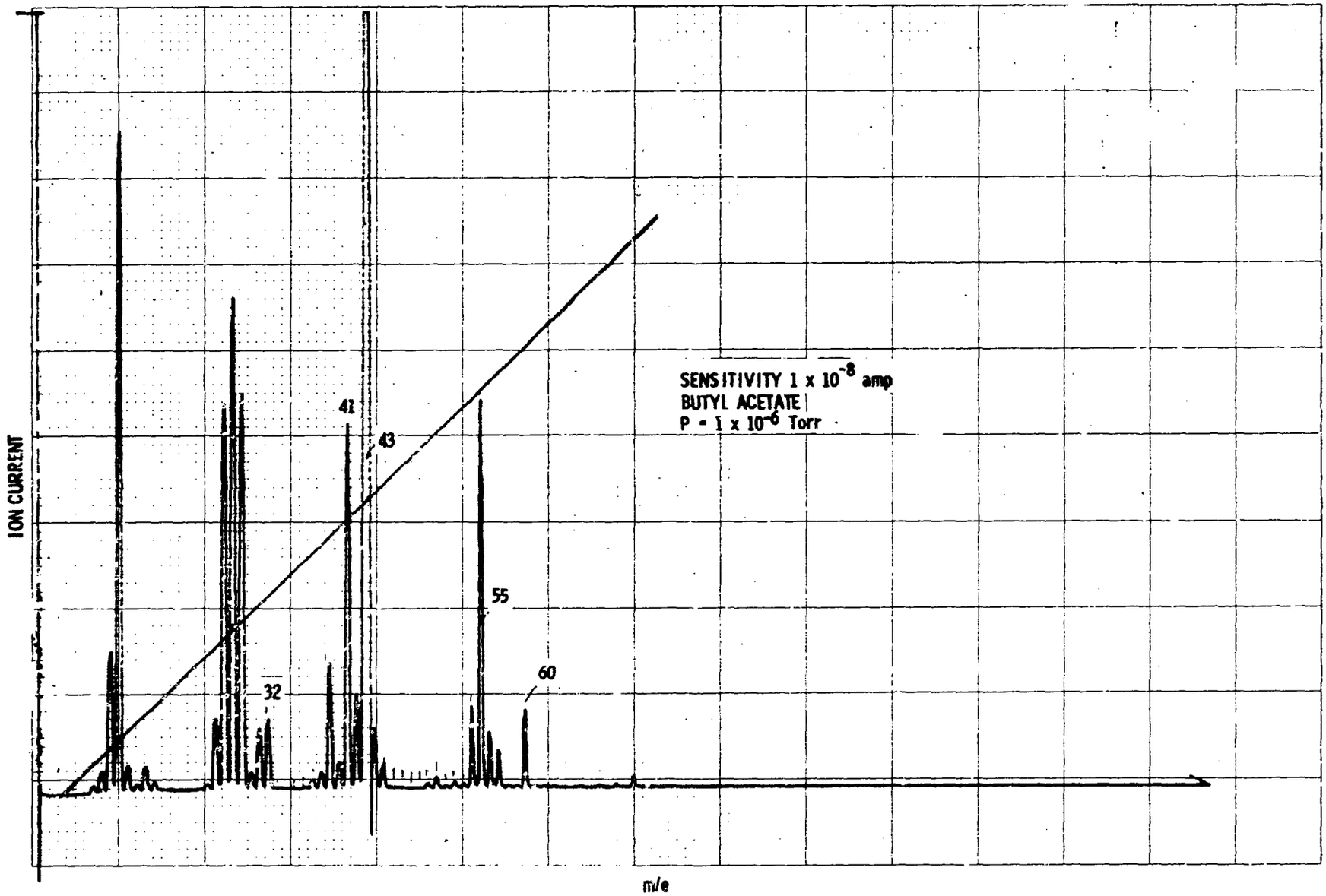


Figure 14. Quadrupole Mass Spectrum of Butyl Acetate

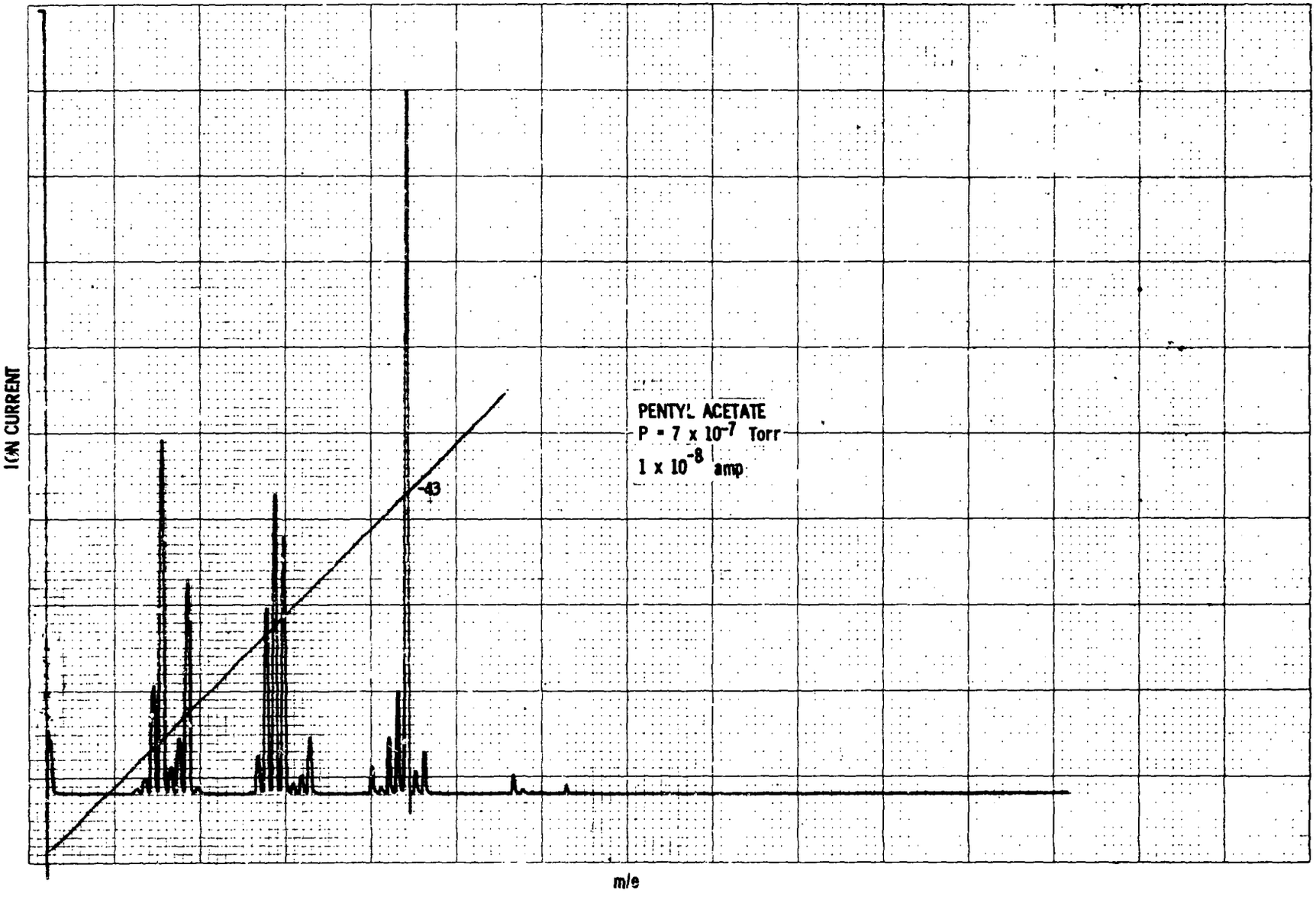


Figure 15. Quadrupole Mass Spectrum of Pentyl Acetate

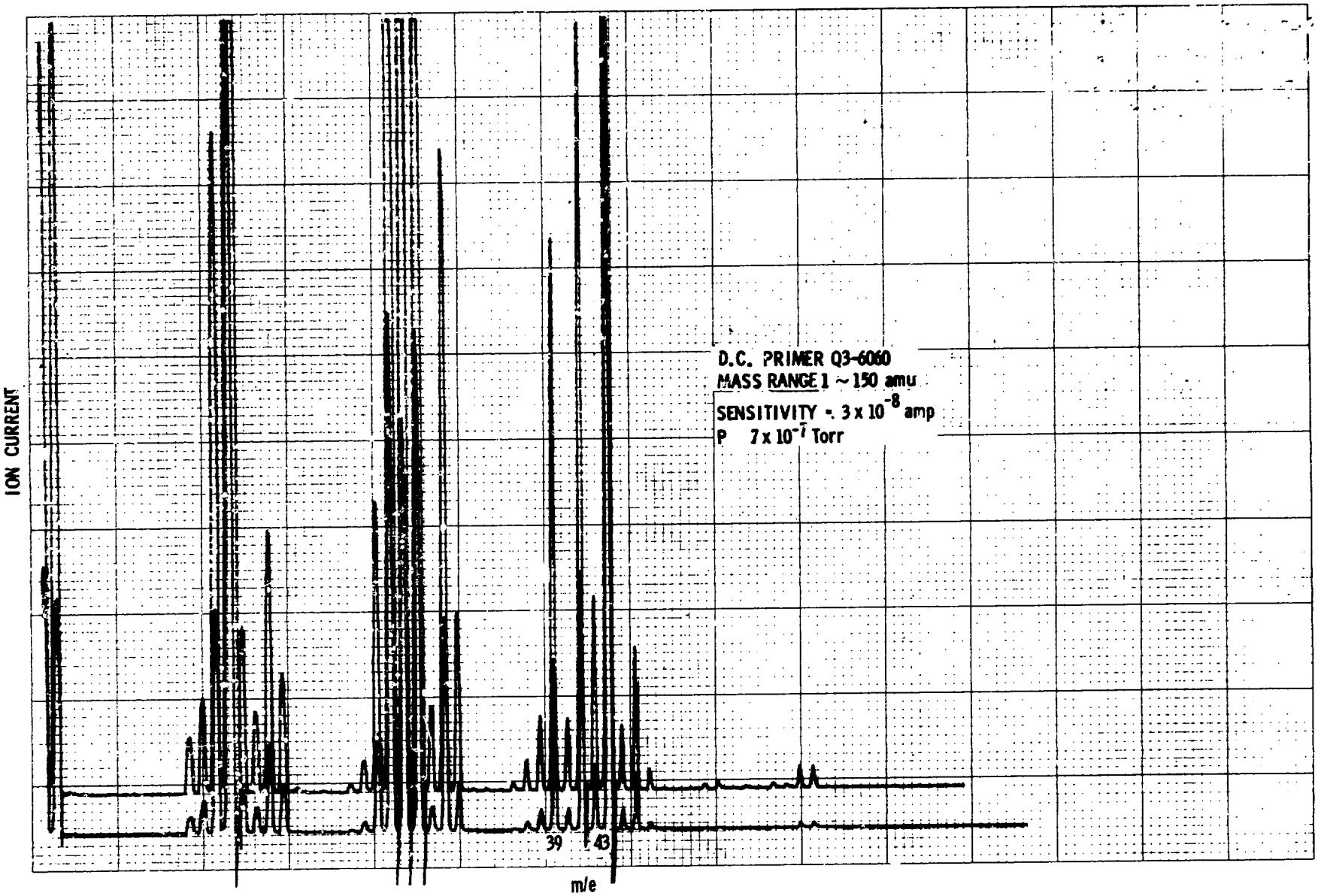


Figure 16. Quadrupole Mass Spectrum of DC Q3-6060 Primer

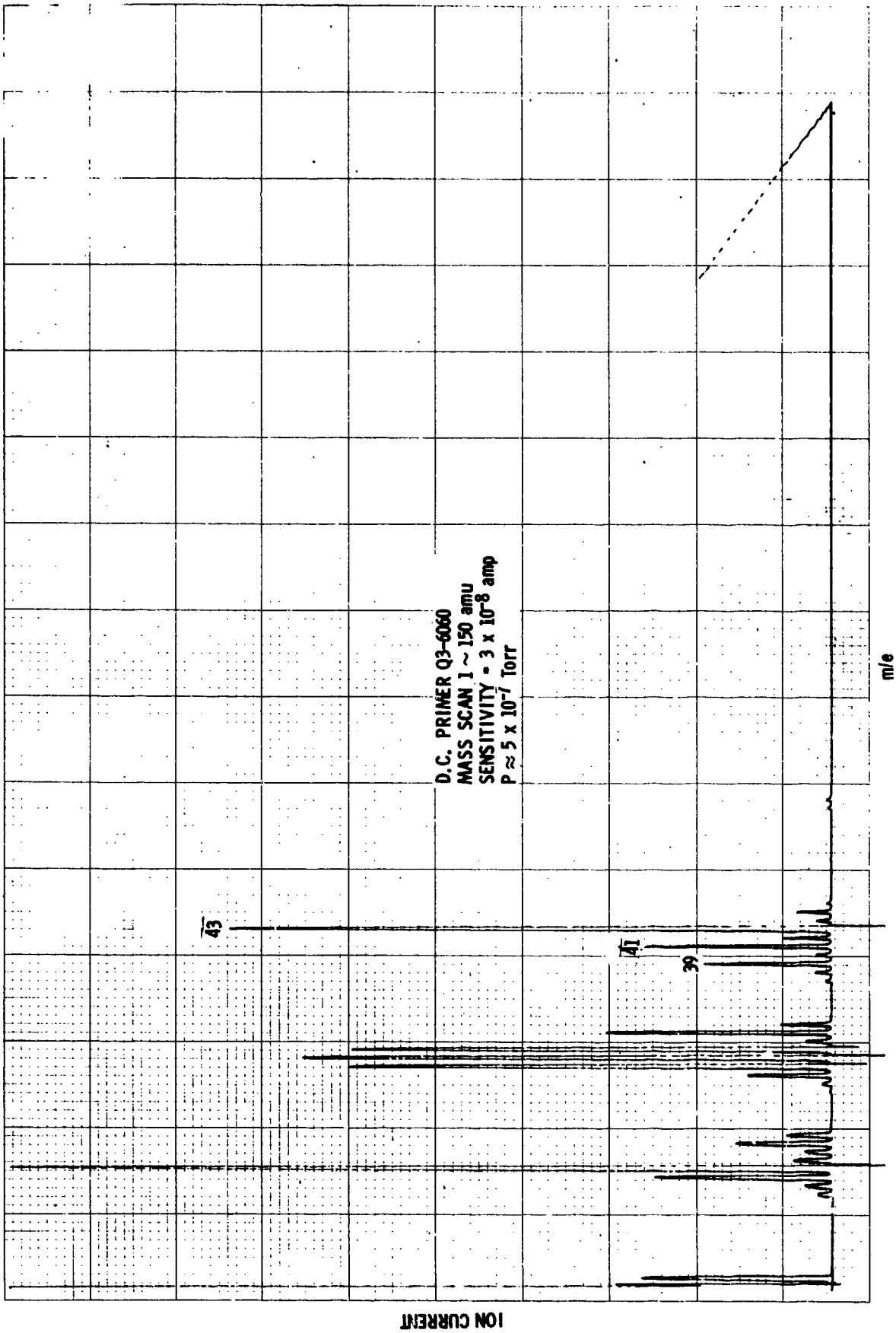


Figure 17. Quadrupole Mass Spectrum of DC Q3-6060 Primer

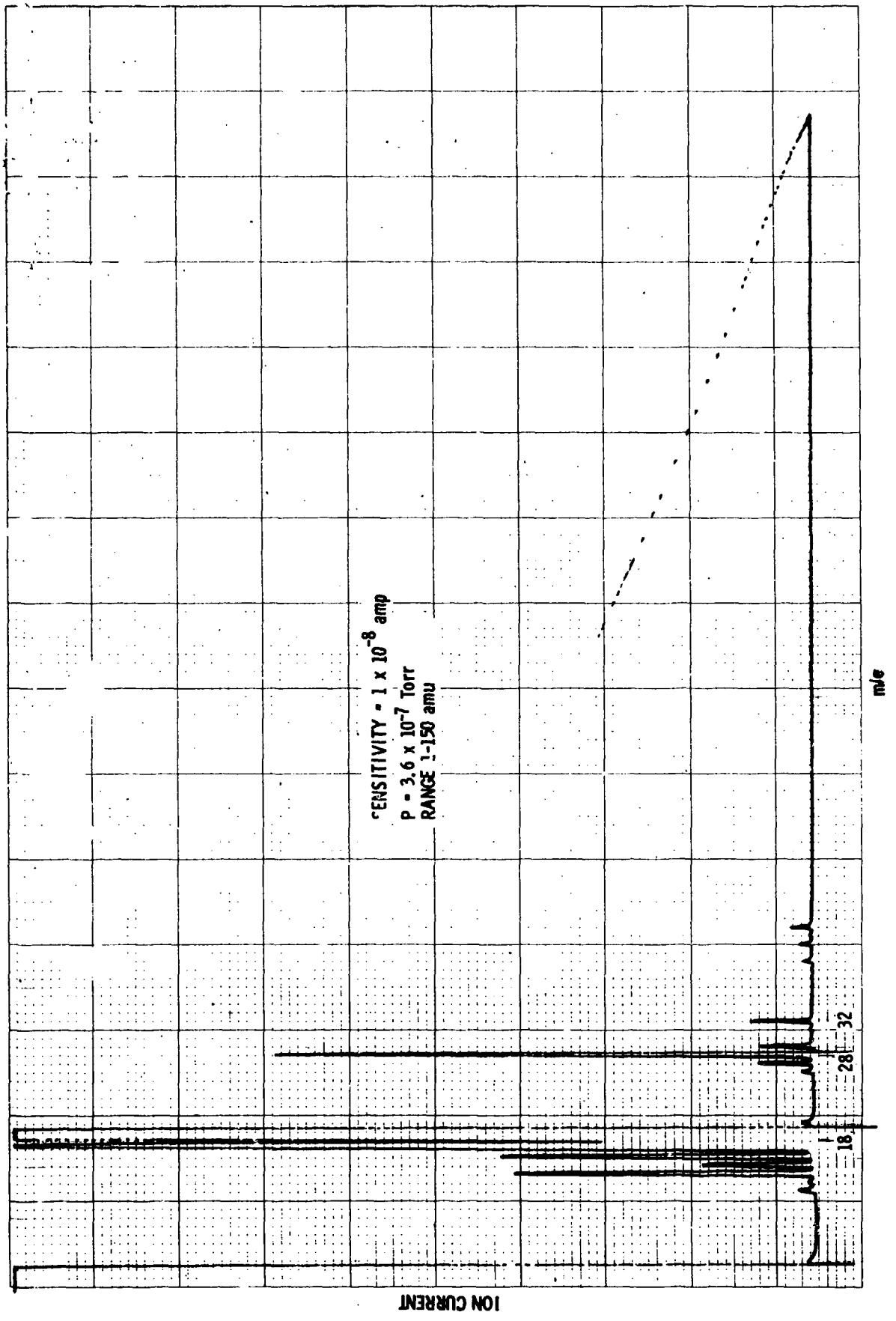


Figure 18. Quadrupole Mass Spectrum of DC 93-500 Encapsulant

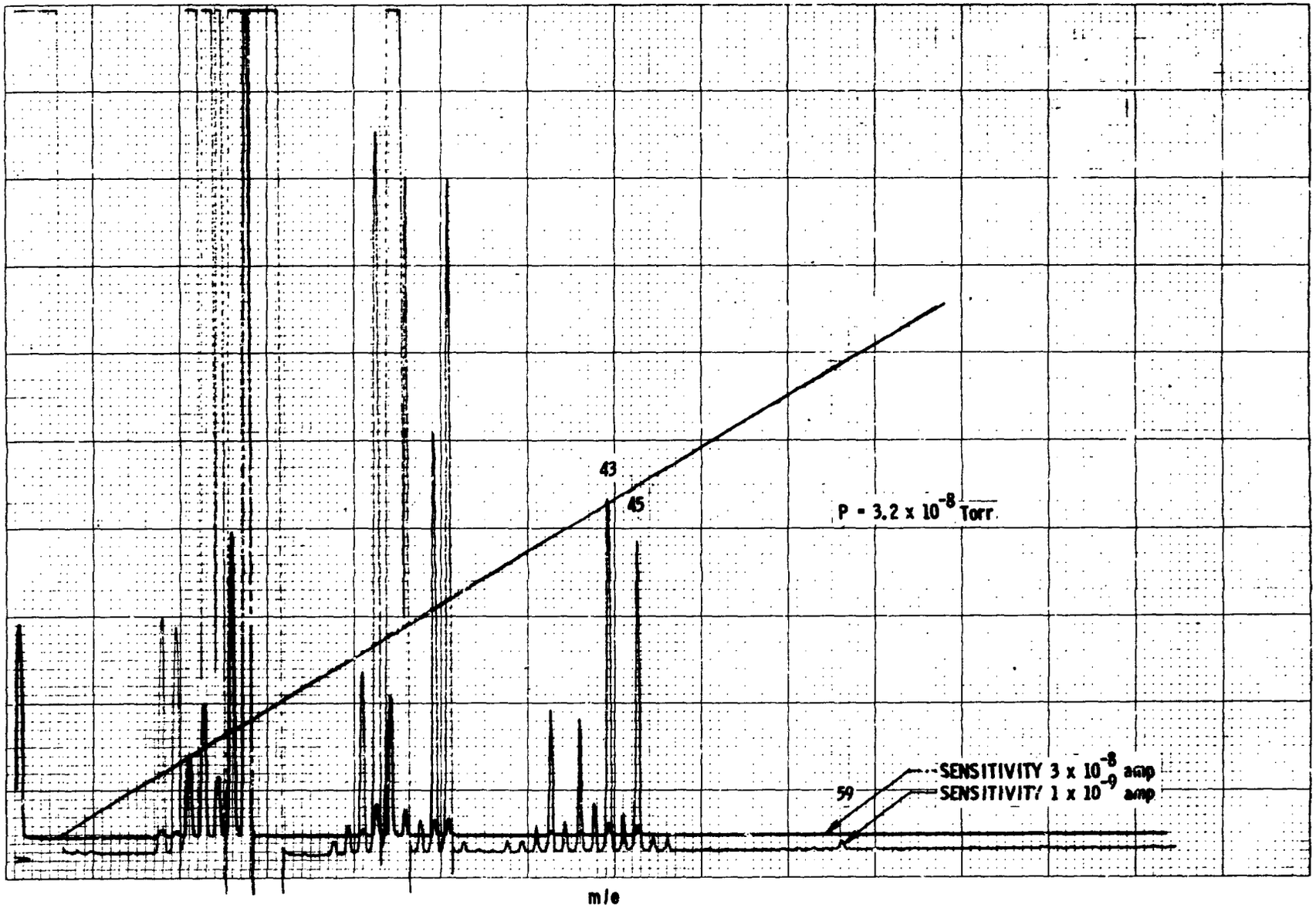


Figure 19. Quadrupole Mass Spectrum of DC 93-500 Curing Agent

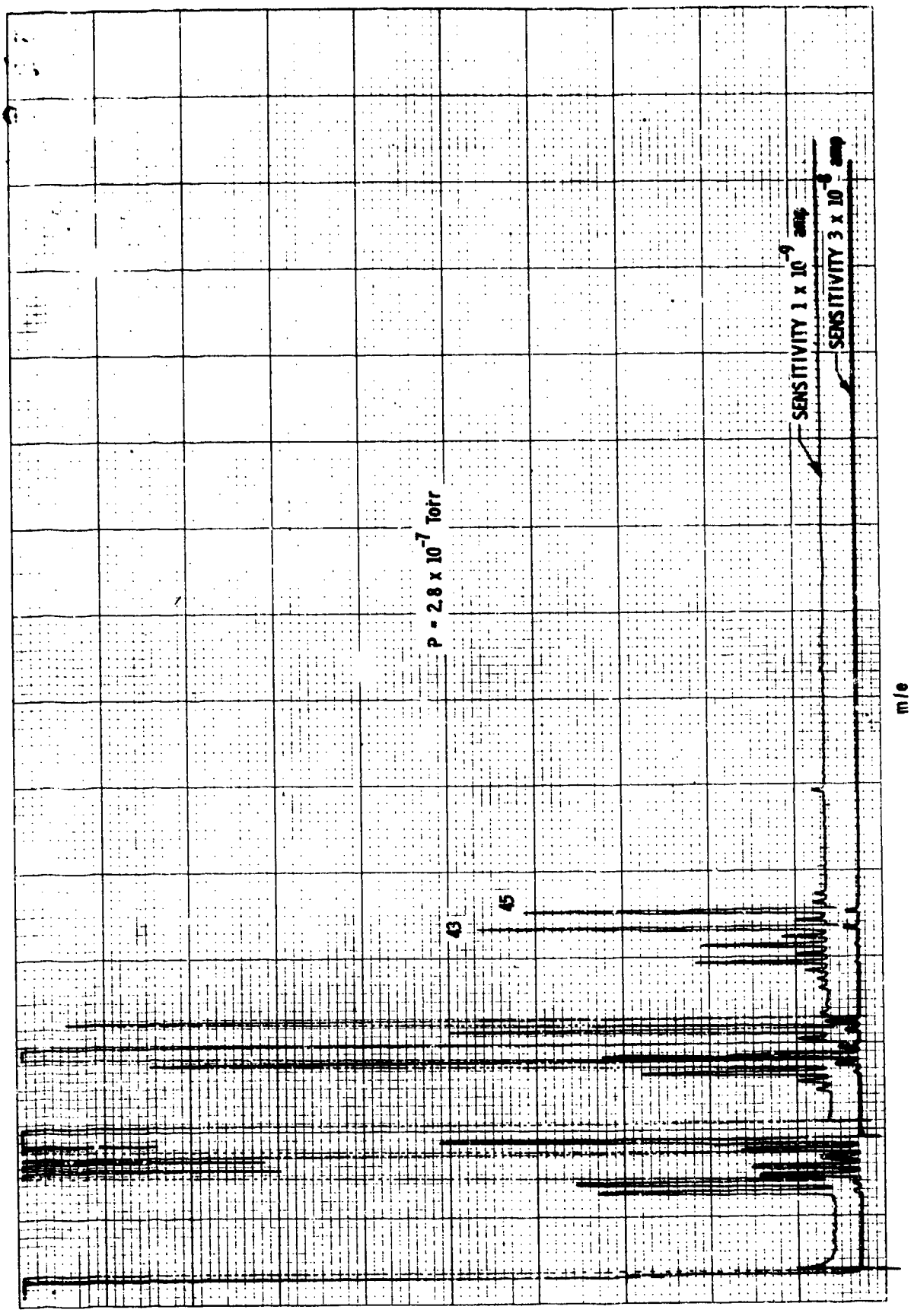


Figure 20. Quadrupole Mass Spectrum of DC 93-500 Curing Agent

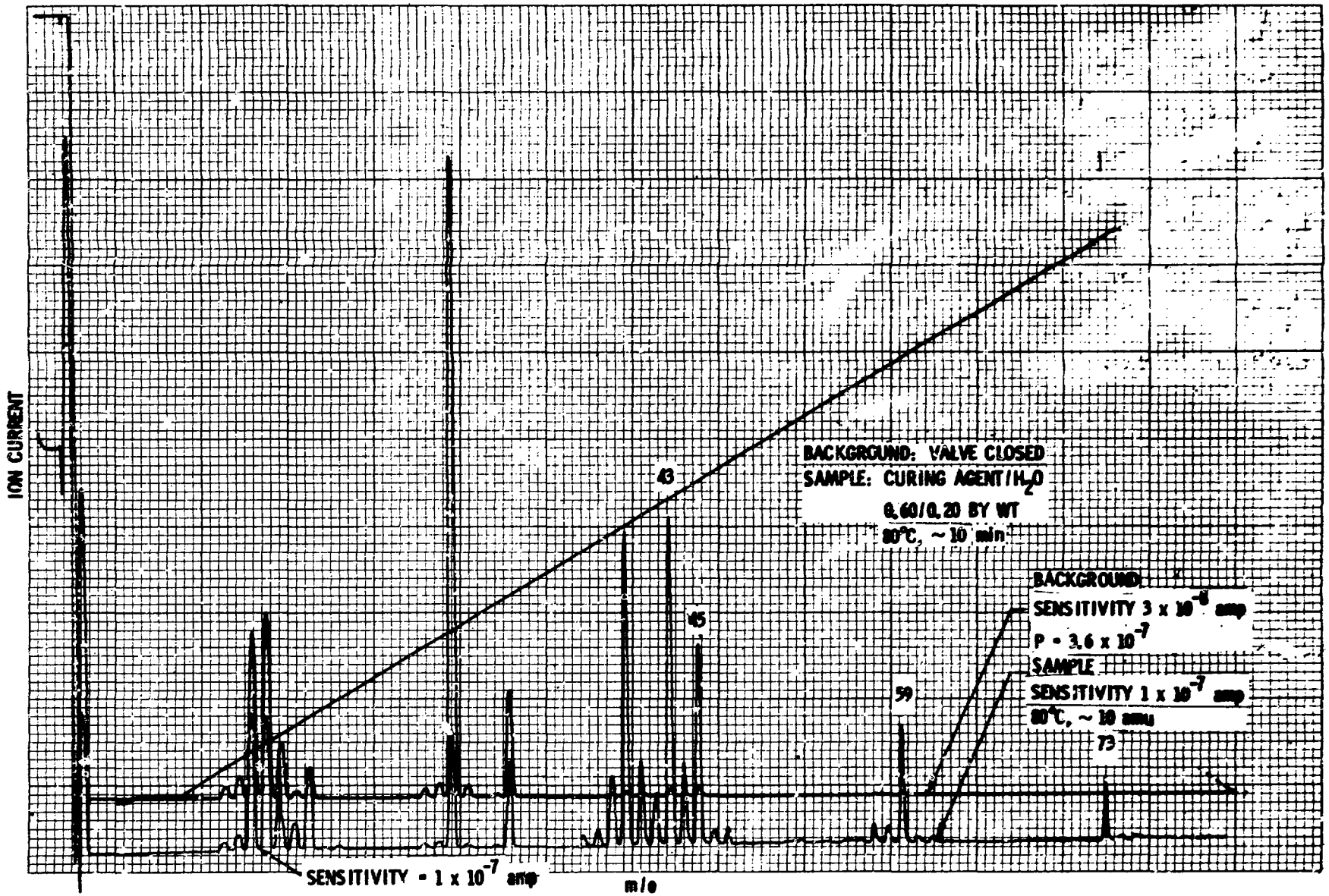


Figure 21. Quadrupole Mass Spectrum of Volatile Reaction Products of DC 93-500 Curing Agent and Water (80°C)